

Anomalous small resistivity and thermopower of strongly compensated semiconductors and topological insulators

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(Dated: December 19, 2012)

In the recent paper we explained why the maximum bulk resistivity of topological insulators (TIs) is so small¹. Using the model of completely compensated semiconductor we showed that when Fermi level is pinned in the middle of the gap the activation energy of resistivity $\Delta = 0.3(E_g/2)$, where E_g is the semiconductor gap. In this paper, we consider strongly compensated n -type semiconductor. We find position of the Fermi level μ calculated from the bottom of the conduction band and the activation energy of the resistivity Δ as a function of compensation K , and show that $\Delta = 0.3(E_c - \mu)$ holds at any $1 - K \ll 1$. At the same time Peltier energy (heat) Π is even smaller: $\Pi \simeq 0.5\Delta = 0.15(E_c - \mu)$. We also show that at low temperatures the activated conductivity crosses over to variable range hopping (VRH) and find the characteristic temperature of VRH, T_{ES} , as a function of $1 - K$.

I. INTRODUCTION

The three-dimensional (3D) topological insulator (TI)²⁻⁶ has gapless surface states, which host a spectrum of quantum transport phenomena^{7,8}. While a number of crystals have been identified to be 3D TIs, most of them are poor insulators and the bulk of TI crystals of substantial size ($> 10\mu\text{m}$) shunts the surface conductivity. The current literature⁹⁻¹⁷ broadly discusses how one can achieve a bulk-insulating state.

Typically as-grown TI crystals are heavily doped n -type semiconductors. To make them insulating they are compensated by acceptors. With increasing compensation $K = N_A/N_D$, where N_D and N_A are the concentrations of monovalent donors and acceptors, the Fermi level shifts from the conduction band to inside the gap and then into the valence band. When compensation of donors is complete, $K = 1$, the Fermi level is in the middle of the gap and the most insulating state of TI is reached. The hope is that for a TI with the gap $E_g \sim 0.3$ eV the resistivity obeys the activation law

$$\rho = \rho_0 \exp(\Delta/k_B T) \quad (1)$$

with activation energy $\Delta = E_g/2 \sim 0.15$ eV, so that at room temperatures and below TI is well insulating.

The typical experimental situation at $K = 1$ is however frustrating¹⁶. In the range of temperatures between 100 K and 300 K the resistivity is activated, but with three times smaller than expected activation energy $\Delta \sim 50$ meV. At $T \sim 100$ K the activated transport is replaced by variable range hopping (VRH) and resistivity grows even slower with decreasing T . Finally, at even smaller $T < 50$ K resistivity saturates around $\rho(T) < 10\Omega\text{cm}$. This means that in spite of complete compensation even at helium temperatures conductance of TI samples thicker than $10\mu\text{m}$ is dominated by the bulk.

In the recent paper¹ we suggest an explanation of anomalously large bulk conductivity of TI at $K = 1$. We assume that both donors and acceptors are shallow and randomly positioned in space. and use theory of a

completely compensated semiconductor (CCS)^{18,19}. This theory is based on the idea that at $K = 1$, when almost all donors and acceptors are charged, random spatial fluctuations of local concentration of impurities result in large fluctuations of charge. Their potential is poorly screened, because of vanishing average concentration $n = N_D - N_A$ of electrons. Huge fluctuations of the random potential bend conduction and valence band edges and in some places bring them to the Fermi level, creating electron and hole puddles, which in turn nonlinearly screen the random potential. As a result, the amplitude of potential fluctuations is limited by $E_g/2$ so that the ground state of completely compensated semiconductor shown in Fig. 1 reminds a network of p - n junctions^{18,19}. Characteristic size of these p - n junctions R for $E_g \sim 0.3$ eV, $N_D = 10^{19} \text{ cm}^{-3}$, the dielectric constant $\kappa = 30$ is $R = 150 \text{ nm} \gg N_D^{-1/3} = 4.6 \text{ nm}^1$, i.e. we deal with a very long range potential. As a result, the resistivity can be dramatically different from the one for the flat bands picture of TI¹. First, at relatively high temperatures activated conductivity is due to electrons and holes activated from the Fermi level to their corresponding classical percolation levels (classical mobility edges), E_e and E_h , in the conduction and the valence bands. According to numerical modelling at $K = 1$ ¹ the activation energy $\Delta \simeq 0.15E_g$, because E_e and E_h are substantially closer to the Fermi level μ than the unperturbed by random potential bottom of conduction band E_c and ceiling of the valence band E_v (Fig. 1a). Second, at low enough temperatures electrons and holes can hop (tunnel) between puddles, so that variable range hopping conductivity replaces activated transport. We showed that the activated resistivity crosses over directly to Efros-Shklovskii (ES) law²⁰

$$\rho = \rho_0 \exp(T_{ES}/T)^{1/2}, \quad (2)$$

where $T_{ES} = Ce^2/k_B\kappa\xi$, e is the electron charge, ξ is localization length of the states with the Fermi level energy and $C = 4.4$ is a numerical coefficient. Together our results for the activated and VRH resistivity estab-

lished the universal upper limit of resistivity $\rho(T)$ one can achieve for a 3D TI compensated by shallow impurities.

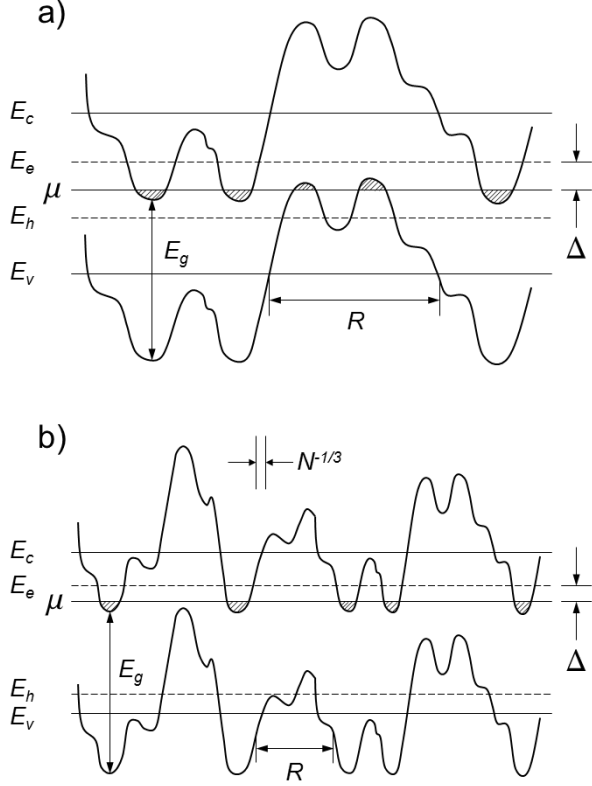


FIG. 1. Energy diagram of a) completely compensated semiconductor ($K = 1$) and b) strongly compensated semiconductor ($1 - K \ll 1$) with the gap E_g . The upper and the lower straight lines indicate the unperturbed positions of the bottom of the conduction band, E_c , and the ceiling of the valence band E_v ; the middle straight line corresponds to the Fermi level μ . Meandering lines represent the band edges, which are modulated by the fluctuating potential of charged impurities, R is characteristic size of potential fluctuations. Percolation levels for electrons, E_e and holes, E_h are shown by dashed lines. Puddles occupied by carriers are shaded. Shallow impurities levels are not shown because they practically merge with band edges.

In this paper, we change our focus from maximum possible bulk resistivity of completely compensated semiconductor at $K = 1$ to the more practical question of dependence of bulk resistivity of strongly compensated semiconductor (SCS) on K at $1 - K \ll 1$. Indeed, with existing methods of growth of TI samples one can not get $K = 1$ exactly and it is important to know how stable $K = 1$ resistivity results are in the case $1 - K \ll 1$. For example, one can ask at which $1 - K$ activation energy Δ is twice smaller than at $K = 1$. For definiteness we consider n -type SCS, where concentration of electrons $n = N_D - N_A \ll N_D$ and $1 - K \ll 1$. We model numerically ground state of such SCS and its resistivity using algorithms similar to Ref.¹. We find that in agreement with analytic theory¹⁸ when $1 - K$ grows screening of random

potential improves and its correlation length R decreases. The amplitude of the random potential decreases as well, hole puddles shrink and eventually vanish and the chemical potential μ moves up, so that $E_c - \mu$ decreases. One can say that with increasing $(1 - K)$ screening happens by bending of the conduction band only while all acceptors remain occupied by electrons and negative. All these changes are illustrated by transition from a) to b) in Fig. 1.

As a result of these changes with growing $1 - K$ the activation energy Δ decreases. We find that the relation $\Delta = 0.3(E_c - \mu)$ obtained in Ref.¹ for $K = 1$ remains valid for $1 - K \ll 1$ (see Fig. 7 below) as well. (In p -type semiconductor where $K = N_D/N_A$ similar relationship $\Delta = 0.3(\mu - E_v)$ takes place.) By $K = 0.97$ the activation energy Δ is at least two times smaller than at $K = 1$. This result shows that achieving maximum resistivity with $\Delta = 0.15E_g$ is problematic. It also explains the origin of large scatter of magnitude of Δ among TI samples¹⁶.

Our prediction that $\Delta = 0.3(E_c - \mu)$ in principle can be directly compared with experiments in TIs. Indeed, for each K the position of the Fermi level ($E_c - \mu$) can be found via measurements of the surface concentration of electrons in the surface gapless state using Shubnikov-de-Haas oscillations.

At low temperatures we find numerically direct crossover from activation to ES VRH. We also find how T_{ES} being correlated with Δ decreases with $1 - K$.

Our assumption of random distribution of impurities is crucial for this theory. Usually for samples made by cooling from melt distribution of impurities in space is a snapshot of the distribution, which impurities have at higher temperature, when diffusion of impurities practically freezes. In semiconductors with a narrow enough gap at this temperature there is a concentration of intrinsic carriers larger than the concentration of impurities. Intrinsic carriers screen Coulomb interaction between impurities, so that impurities remain randomly distributed in space. At lower temperatures when intrinsic carriers recombine impurities are left in random positions^{18,21}. If diffusion freezes at $T \sim 1000K$ it is reasonable to assume that impurities are randomly positioned in a semiconductor with $E_g \leq 0.3$ eV. This justifies the use of this theory for typical TIs. Our results are applicable to other narrow gap semiconductors, for example, to InSb. Historically, large effort was made to make InSb insulating via strong compensation. The goal was to improve characteristics of InSb based photo-detectors. Results were again frustrating: the dark resistivity was too small. Our results are in a reasonable agreement with transport experimental data for InSb^{22,23}.

The plan of the paper is as follows. In section II we formulate the model, explain the algorithm of numerical simulation of the pseudo-ground state and present results for the density of states (DOS). In section III we present our algorithm for computation of hopping conductivity, analyze our results and arrive at a small activation energy of conduction band resistivity $\Delta = 0.3(E_c - \mu)$. We also

evaluate the localization length of states close to Fermi energy and estimate characteristic temperature of ES law T_{ES} . In Sec. IV we estimate the thermopower of strongly compensated semiconductor and show that Peltier energy (heat) $\Pi \simeq \Delta/2 = 0.15(E_c - \mu)$.

II. THE MODEL, PSEUDOGROUND STATES AND THE DENSITY OF STATES

To model a heavily doped SCS we create a cube filled by 20000 donors and 20000K acceptors that are randomly positioned in space. We numerate all donors and acceptors by index i and use $n_i = 0$ or 1 for number of electrons residing on a donor or an acceptor. In addition we use a variable f_i to discriminate between donors ($f_i = 1$) and acceptors ($f_i = -1$). The Hamiltonian of our system is

$$H = \sum_i \frac{E_g}{2} f_i n_i + \sum_{\langle ij \rangle} V(r_{ij}) q_i q_j. \quad (3)$$

where $q_i = (f_i/2 - n_i + 1/2)$ is the net charge of site i and all energies are defined relative to the Fermi level. The first term contains the difference between the energies of shallow donors and acceptors which for the case of shallow impurities is very close to the semiconductor gap E_g . The second term of H are the sum of interaction energies of charged impurities. If two impurities are at distance $r \gg a_B$, where a_B is the Bohr radius of impurity states, one can use the Coulomb interaction $V(r) = e^2/\kappa r$. For a pair of empty donors, one donor shifts down the energy of the electron on the other by energy $V(r) = -e^2/\kappa r$. This classical form for $V(r)$ is good for a lightly doped SCS. But in a heavily doped SCS, where $a_B > N_D^{-1/3}$ most impurities have at least one neighbor at distance $r < a_B$ and quantum mechanical averaging over electron wave function becomes important. (This is why uncompensated heavily doped semiconductor is a good metal). For example, such a donor pair cannot create a state deeper than one of the helium-like ion with binding energy $4E_B$, where $E_B = e^2/2\kappa a_B$ is the binding energy of the shallow donor state. Here we deal with heavily doped SCS, where $(E_c - \mu) > 4E_B$ and quantum effects limit the role of short range potential. To model such a case we continue to use classical Hamiltonian Eq. (3), but truncate the Coulomb potential to $V(r) = e^2/\kappa(r^2 + a_B^2)^{1/2}$. Note that Eq. (3) does not include the kinetic energy of electrons and holes in conduction and valence bands and, therefore, aims only at description of the low temperature ($k_B T \ll E_g$) physics of SCS.

Below we use dimensionless units, for r , a_B , H , E_g , $k_B T$ measuring all distances in units of $N_D^{-1/3}$ and all energies in units of $e^2 N_D^{1/3}/\kappa$. Thus, Eq. (3) now can be understood as dimensionless, where $E_g \gg 1$ and $V(r) = (r^2 + a_B^2)^{-1/2}$. For TI with the energy gap 0.3 eV, $\kappa = 30$ and $N_D = 10^{19} \text{cm}^{-3}$, $N_D^{-1/3} = 4.6 \text{ nm}$, $e^2 N_D^{1/3}/\kappa = 10$

meV, so that dimensionless $E_g = 30$. We could not model $E_g = 30$, because in this case the very large correlation length of long range potential, R , leads to large size effect. Instead, we run more modest $E_g = 15$, for which the size effect requires extrapolation only for $K = 1^1$. Our goal is to find activation energy Δ and estimate T_{ES} as functions of K or μ .

We search for the set $\{n_i, f_i\}$ that minimizes H and use such a set to calculate the DOS and the conductivity. We start from the neutral system of all populated by electrons (negatively charged) acceptors ($n_i = 1, q_i = -1$), of equal number of randomly chosen 20000K empty (positively charged) donors ($n_i = 0, q_i = 1$), and of 20000(1 - K) filled (neutral) donors ($n_i = 1, q_i = 0$). Charged donors and acceptors create a random potential whose magnitude exceeds E_g . In order to screen the Coulomb potential fluctuations, some electrons leave acceptors for donors. At any stage of this process there are two types of occupied states - neutral donors and negatively charged acceptors, and two types of empty states - positively charged donors and neutral acceptors, respectively. Electrons may hop from an occupied impurity to an empty one. If the proposed move lowers the total system energy H , then it is accepted, otherwise it is rejected. To check whether H goes down, for a given electron occupation numbers $\{n_i, f_i\}$ it is convenient to introduce the single-electron energy state, ε_i , at a given impurity i

$$\varepsilon_i = \frac{E_g}{2} f_i - \sum_{j \neq i} V(r_{ij}) q_j. \quad (4)$$

For all i, j with $n_i = 1$ and $n_j = 0$ we check that ES pseudo-ground state stability criterion is satisfied:

$$\varepsilon_j - \varepsilon_i - V(r_{ij}) > 0. \quad (5)$$

If this criterion is not satisfied we move electron from impurity i to j and recalculate all ε_i . This process is done by looping all possible pairs of impurities i, j with $n_i = 1$ and $n_j = 0$ and is continued until no single-electron transfers are possible that lower H . The final arrangement of electrons can be called a pseudo-ground state, because higher stability criteria of ground state are not checked. Pseudo-ground states are known to describe properties of real ground state pretty well^{18,24}. Results below are obtained at $E_g = 15$, $a_B = 1$ for $K = 1, 0.99, 0.98, 0.97, 0.96$ and 0.95 and are averaged over 100 realizations of impurities coordinates.

For a pseudo-ground state we find Fermi energy μ as a half distance between minimum empty and maximum occupied energy ε . Fig. 2 shows how the Fermi level $\mu(K)$ shifts from the middle of the gap towards the conduction band bottom with growing $1 - K$. At $1 - K > 0.01$ this dependence is in reasonable agreement with prediction of single band theory (the theory which ignores valence band and acceptors)¹⁸ that $E_c - \mu = A(1 - K)^{-1/3}$. Note, however that for heavily doped SCS the coefficient $A_h \simeq 1.4$ is twice smaller than the coefficient $A_l \simeq 2.8$ obtained in Ref.¹⁸ for a lightly doped SCS, where $a_B \ll 1$.

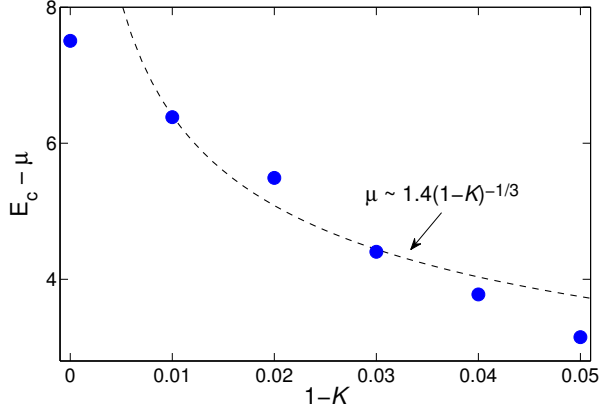


FIG. 2. (Color online) Fermi level μ as a function of $1 - K$ for $a_B = 1$ and $E_g = 15$. The size of dots characterizes the uncertainty.

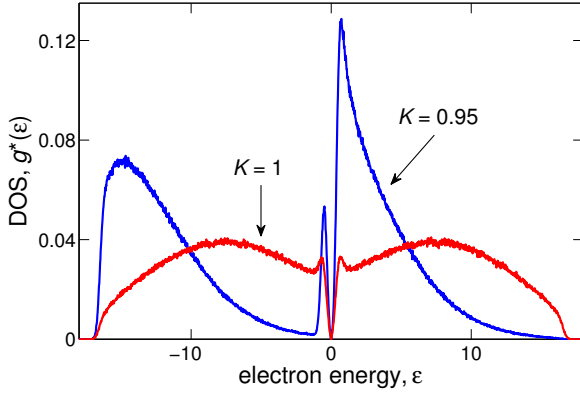


FIG. 3. (Color online) Dimensionless single-electron DOS $g(\varepsilon)$ in units $[(1 + K)N/(e^2 N^{1/3}/\kappa)]$ as a function of ε calculated from the Fermi level for $a_B = 1$ and $E_g = 15$ at $K = 0.95$ (blue) and 1 (red). Impurity states with $\varepsilon < 0$ are occupied and with $\varepsilon > 0$ are empty. At $K = 1$ the total DOS of impurities has donor-acceptor symmetry, which is lost with growing $1 - K$.

In this case the short range Coulomb interaction at distances $r \ll N^{-1/3}$ leads to an additional contribution to μ of the same order of magnitude.

To confirm our understanding of results for $1 - K > 0.01$ we obtained same results for the position of Fermi level μ (and DOS of donors and conductivity, see below) running a simplified one band model where all acceptors are assumed to be negative. Such program is similar to the classical impurity band program used in Chapter 14 of Ref.¹⁸, but uses the redefined $V(r)$.

The resulting DOS of impurities is shown in Fig. 3 for $K = 1$ and $K = 0.95$. $g^*(\varepsilon)$ is the DOS in the units of $(1 + K)N_D/(e^2 N_D^{1/3}/\kappa)$ and is normalized to unity.

At $K = 1$, almost constant symmetric DOS between $-E_g = -15$ to $E_g = 15$ reflects practically uniform dis-

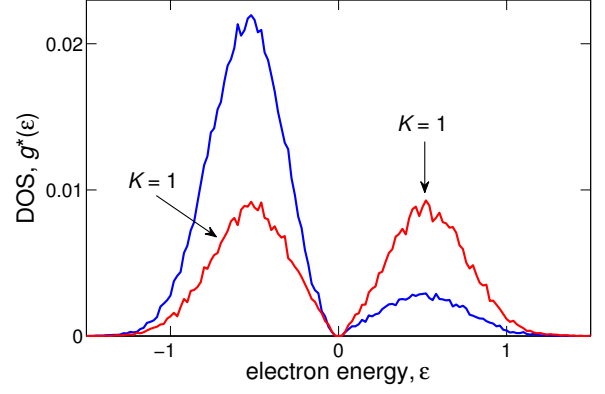


FIG. 4. (Color online) Dimensionless DOS $g(\varepsilon)$ for neutral (occupied by electrons) donors at $\varepsilon < 0$ and neutral (empty) acceptors at $\varepsilon > 0$ as a function of energy ε calculated from the Fermi level for $a_B = 1$ and $E_g = 15$ at $K = 1$ (red), 0.99 (green) and 0.98 (blue).

tribution of random potential from $-E_g/2$ to $E_g/2$ and of band edges E_c and E_v between 0 to E_g and between 0 to $-E_g$ correspondingly (see Fig. 1a). In the middle (at the Fermi level) one sees the ES Coulomb gap²⁰.

At $K < 1$ the DOS of impurities loses donor-acceptor symmetry it has at $K = 1$. As mentioned in introduction (see Fig. 1) with growing $1 - K$ acceptors become all filled and disengaged from screening. Acceptor DOS (leftmost peak) splits from the donor one, which in turn has two peaks separated by the Fermi level. The large right peak belongs to empty donors, while the small and narrow left peak belongs to occupied donors. The donor peaks are separated by the ES Coulomb gap.

Growing with $1 - K$ disengagement of acceptors from screening is also illustrated in Fig. 4, where we show DOS $g(\varepsilon)$ for neutral donors and acceptors. If at $K = 1$ the total number of electrons and holes in puddles are equal, with the growing $1 - K$ the total number of electrons in electron puddles grows, while the total number of holes in hole puddles decreases. Thus, at $1 - K \geq 0.02$ valence band practically plays no role in screening.

III. NUMERICAL MODELLING OF HOPPING CONDUCTIVITY

Once the energies $\{\varepsilon_i\}$ are known, we evaluate the resistivity using the approach of the Miller-Abrahams resistor network¹⁸. Each pair of impurities i, j is said to be connected by the resistance $R_{ij} = R_0 \exp[2r_{ij}/\xi + \varepsilon_{ij}/k_B T]$, where the activation energy ε_{ij} is defined¹⁸ as follows:

$$\varepsilon_{ij} = \begin{cases} |\varepsilon_j - \varepsilon_i| - V(r_{ij}), & \varepsilon_j \varepsilon_i < 0 \\ \max[|\varepsilon_i|, |\varepsilon_j|], & \varepsilon_j \varepsilon_i > 0. \end{cases} \quad (6)$$

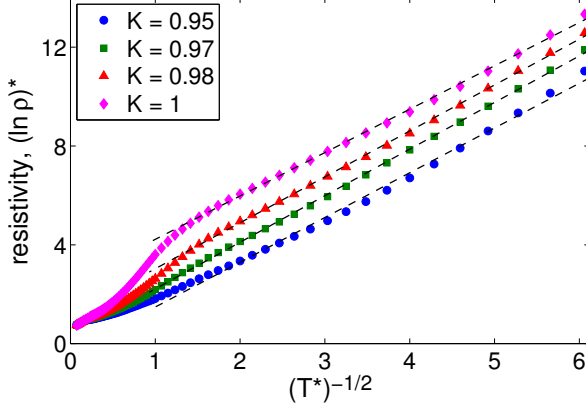


FIG. 5. (Color online) The temperature dependence of the resistivity in the whole temperature range $200 > T^* > 0.03$. The dimensionless resistance $(\ln \rho)^*$ is plotted against $(T^*)^{-1/2}$ to illustrate that the resistivity follows the ES law at low temperatures. The dashed lines are the best linear fits.

The resistivity of the system as a whole is found using a percolation approach. Specifically, we find the minimum value R_c such that if all resistances R_{ij} with $R_{ij} < R_c$ are left intact, while others are eliminated (replaced with $R = \infty$), then there exists a percolation pathway connecting opposite faces of the simulation volume. The system resistivity $\rho(T)$ is defined as $R_c N^{-1/3}$. Here we concentrate on exponential term of resistivity ρ ignoring details of the prefactor¹⁸.

For $K=0.95, 0.97, 0.98$ and 1 at $a_B = 1$ and $E_g = 15$, the computed dependence of $(\ln \rho)^* = (\xi/2) \ln R_c/R_0$ is shown as a function of $(T^*)^{-1/2}$ in the huge range of temperatures $200 > T^* > 0.03$ in Fig. 5. Here $T^* = 2k_B T/\xi$ is yet another dimensionless temperature. These notations are introduced to exclude any explicit dependence on ξ . It is seen that at low temperatures $0.3 > T^* > 0.03$, resistivity is well described by ES law Eq. (2) (with $C \simeq 4.4$ at $K = 1$). The higher temperature range $200 > T^* > 1$ is plotted separately as a function of $1/T^*$ in Fig. 6b. We find two activated regimes of hopping conductivity. At high temperatures $200 > T^* > 50$ we see the large activation energy $E_a \sim (E_c - \mu)$ and at intermediate temperatures range $E_g > T^* > 1$ we see much smaller activation energy $\Delta = 0.3(E_c - \mu)$.

The first activation energy E_a does not have any physics meaning for a real SCS, because at $k_B T > E_g$ conductance of SCS is actually not due to hopping, but due to high energy free carriers, which are not taken into account by energy Eq. (3) (see Ref.¹). In contrary to E_a , the second activation energy $\Delta = 0.3(E_c - \mu)$ makes full physics sense and should be seen in a real experiment. The origin of this activation energy for the hopping transport is also explained in Chapter 8 of Ref.¹⁸). At $T \ll E_g$ electrons optimize their conductivity using for hopping impurities energetically close to the Fermi level. Eventually at very low temperatures such optimization

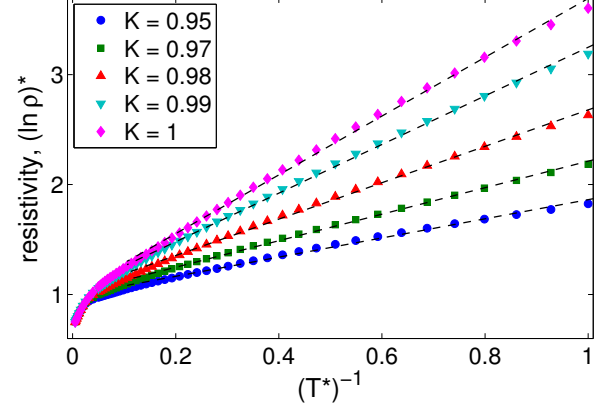


FIG. 6. (Color online) The temperature dependence of the resistivity in the high temperature range $200 > T^* > 1$. The dimensionless resistance $(\ln \rho)^*$ is plotted against $(T^*)^{-1}$ to illustrate that the resistivity is activated at high temperatures. The dashed lines are the best linear fits.

leads to ES conductivity. However, when donor energies are slowly modulated by the long range potential there are large areas which do not have donors with energies close to the Fermi level and tunneling through them is slow. Therefore, there is a range of temperatures where, electrons use only nearest neighbor donors for hopping, while activating to donors located at the percolation level of nearest neighbor percolation. We find activation energy from the Fermi level to the nearest neighbor percolation level studying hopping activation energy Δ . In a heavily doped semiconductor this energy is not discriminable from activation energy of electrons from the Fermi level to the conduction band percolation level E_c . (Of course, holes are activated from the Fermi level to their percolation E_h as well so that $\Delta = 0.3(\mu - E_h)$).

We verified that hopping conduction modelling correctly predicts activation energy of the band transport by direct of calculation of the percolation level E_c . For this purpose we created a cubic lattice with a small lattice constant $N^{-1/3}/3$. At every site of this lattice we calculated potential of all charged impurities and then found lowest energy E_e at which percolation over this lattice takes place. Activation energy of the band transport was again close to $\Delta = 0.3(E_c - \mu)$. This result is also close to one obtained in Ref.²⁵ based on estimate of percolation level for a generic random long range potential¹⁸.

In Fig. 7 we plot the function $\Delta(E_c - \mu)$ for all the values $\mu(K)$ obtained for $K = 1, 0.99, 0.98, 0.97, 0.96, 0.95$ we studied. We see that equation $\Delta \simeq 0.3(E_c - \mu)$ holds well for all K in this interval.

So far we emphasized results, which do not explicitly depend on ξ . Actually, a magnitude of ξ is necessary to calculate T_{ES} . We argue now that in a TI ξ is quite large leading to prominent role of VRH. If electron with energy close to the Fermi level were tunneling from an electron puddle to a distant one along the straight line it would

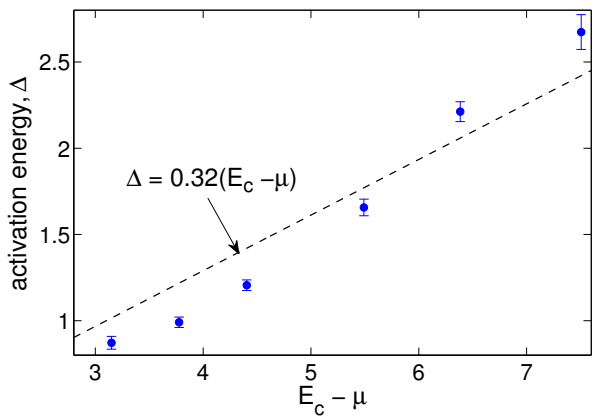


FIG. 7. (Color online) The activation energy Δ at $K = 1.0, 0.99, 0.98, 0.97, 0.96$, and 0.95 (from right to left). The dashed line is the best linear fit $\Delta \simeq 0.3(E_c - \mu)$

tunnel through high barriers and its wave function would decay with $\xi \ll a_B$. Actually, a tunneling electron can use the same geometrical path as a classical percolating electron with energy Δ above the Fermi level which avoid large barriers. We assume that along such a path tunneling barriers V are uniformly distributed in the range $0 \leq V \leq \Delta$ and neglect contribution of curvature of this path into action. Integration over V then gives (from here on we return to normal units) $\xi = \hbar/(8m\Delta/9)^{1/2}$ and $k_B T_{ES} = 4.2(e^2/\kappa\hbar)(m\Delta)^{1/2}$. For a TI with $a_B = N_D^{-1/3}$ we get $T_{ES} = 4.2[(e^2 N_D^{1/3}/\kappa)\Delta]^{1/2}$. For Δ varying between 1 and $2.5 e^2 N_D^{1/3}/\kappa$ as shown in Fig. 7 T_{ES} changes from 4.2 to $6.6 e^2 N_D^{1/3}/\kappa$. For $\kappa = 30$, $N_D = 10^{19} \text{cm}^{-3}$ $e^2 N_D^{1/3}/\kappa k_B \simeq 100$ K and T_{ES} varies from 420 to 1050 K. In order to study VRH in TI samples experimentally one has to deal with large enough samples, where surface conductance is smaller than the bulk one²⁶.

IV. THERMOPOWER

In the recent paper²⁸ the authors studied activation energy of the bulk resistivity of series of samples of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ with different x and, therefore, different positions of the Fermi level in the TI gap. They found that when the Fermi level sinks into the gap the activation energy of resistivity Δ grows and reaches maximum at 40 meV and then decreases. The increase of the activation energy Δ on both sides of the maximum is accompanied by the increase of the absolute value of the thermopower S . However, near the maximum of Δ the thermopower abruptly changes its sign. These findings in agreement with what one can expect when a semiconductor goes through the point of complete compensation. Here we would like to concentrate on the maximum absolute value

of the thermopower, for example, at n -type side of the maximum.

It is known that for flat bands n -type semiconductor with the Fermi level μ inside its gap the thermopower $S = \Delta/eT$, where the activation energy $\Delta = E_c - \mu$. For banded bands of a strongly compensated n -type semiconductor one could think that $S = \Delta/eT$, where the activation energy $\Delta = E_e - \mu$ is determined by activation to percolation level E_e . Actually it was argued²⁹⁻³¹ that the Peltier energy (heat) $\Pi = eTS$ is determined by the average potential energy of electrons (conduction band bottom) along most conducting one-dimensional percolation paths, $\Pi = \langle E - \mu \rangle$. (We call a percolation path any line, where potential energy of electron is smaller than E_e and we call a set of least resistive of these paths, which carry most of the current, as most conducting percolation paths.) Thermopower of an open circuit following an individual percolation path can be obtained by integrating $E - \mu$ along this path. Among two parallel paths connecting points A and B, the more resistive one has somewhat larger open circuit thermopower and, therefore, drives circular current back through the least resistive one. This current reduces thermopower of the resistive path so that voltage between A and B is determined by the more conducting path.

If probability distribution of potential energy E on most conducting paths is the same as for unconditional probability distribution of E , which we call DOS $g(E)$ above, we can use $g(E)$ to calculate Π and S . For example, in the case of a constant $g(E)$ for $\mu < E < E_e$ we get $E_S = \langle E - \mu \rangle = \Delta/2 = (E_e - \mu)/2$. This conclusion was confirmed by the numerical experiment²⁹ for the case of a constant $g(E)$.

In a strongly compensated semiconductor one can use real $g(E)$ found above. For example, at $K = 0.95$ one can use Fig. 2 to find that $\Delta = E_e - \mu \simeq 3$. Then using DOS shown at Fig. 3 one can check that the average energy in the range between in the interval $0 < E < 3$ is $\langle E - \mu \rangle \simeq \Delta/2 = 1.5$. Thus, our simple approximate prediction is that $\Pi \simeq \Delta/2 = E_g/12$. It is valid for all $K \leq 0.98$ we studied. In the future work we plan to verify this prediction by a numerical calculation of the thermopower as a function of K for potential created by donors and acceptors in strongly compensated semiconductor, which we generated in the modelling above.

For the data of the paper²⁸ our prediction means that at $T = 50\text{K}$ the largest thermopower $S = \Pi/eT$ observed should be of the order $25\text{mV}/50\text{K} = 0.5 \text{ mV/K}$ in a good agreement with observed value $S = 0.4 \text{ mV/K}$.

ACKNOWLEDGMENTS

We are grateful to Brian Skinner with whom this work was started, for reading the manuscript and helpful advices. We acknowledge useful discussions with A. Akrap, Y. Ando, J. Kakalios and I. P. Zvyagin. T. Chen was partially supported by the FTPI.

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